A Comparative Study of the Semipermeable Membranes of Copper Ferrocyanide and Nickel Ferrocyanide.

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH A REQUIREMENT FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

BY

LLOYD VAN DOREN

BALTIMORE

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A COMPARATIVE STUDY OF THE SEMIPERMEABLE MEMBRANES OF COPPER FERROCYANIDE AND NICKEL FERROCYANIDE.

INTRODUCTION.

A study of artificial semipermeable membranes has been in progress, by various investigators, for more than half a century.

The true nature of such membranes, however, was very little understood until Pfeffer took up the osmotic pressure problem. And that he had a clear conception of the nature of semipermeable membranes, and of a possible explanation of the passage of water through them is shown by the following; "Ferrocyankupfer ist, wie vielleicht alle Colloide, wasserhaltig; bei 100°C getrocknet enhält es nach Rammelsberg), 7 Aequivalente Wasser, womit natürlich nicht ausgeschlossen ist, das der Niederschlag vor dem Trocknen eine weitere, lockerer gebundene Wassermenge einschloss, Wie Graham) mittheilt, fällt Ferrocyankupfer aus concentrirten Lösungen der Componenten als fast farblose Gallerte nieder, welche erst bei weiterem Wasserzusatz die gewöhnliche rothbraune Farbe durch Wasseraufnahme erlangt. Es ist hier an einem bestimmten Beispiel die verbreitete Erscheinung demonstrirt, das einem wasserhaltigen Niederschlage durch eine Salzlösung ein gewisser Theil seines chemisch gebundenen Wassers entzogen werder kann. Wenn aber eine aus solchem Niederschlag bestehende Membran Salzlösung das Wasser trennt;— eine Wasserbewegnung durch die substanz selbst, dass durch die Tagmen unserer Neiderschalgsmembran zum Salze hin eintreten während ein entgegen gesetzter Uebertritt von Salz nicht erforderlich ist."[1] The recent detailed study,[2] by Prof. Morse in this laboratory, of the very difficult problem of osmotic pressure, and its relation to the Laws of Boyle and Gay-Lussac, has demonstrated that the transference of water through the membrane is dependent upon its *colloidal nature.* (The study, thus far, has been conducted with solutions—of various concen-

1. Pfeffer's Osmotische Untersuchungen.
2. This study has extended over a period of twelve years.

trations, based on the *weight normal* standard, of Cane Sugar, Glucose, Mannite, Potassium Chloride and Barium Chloride.)

The work has shown that the membrane investigated exhibits in the presence of solutions of certain substances—strong electrolytes—a marked deterioration, and as a consequence loses one of the most important characteristics of a semi-permeable membrane; i'e, *inertness* in the presence of a solution of the substance whose osmotic pressure is to be determined. The cause of this deterioration seems to be a coagulation of the colloid caused by the substance in solution in contact with it.

The work of Pappada.[3]

Pappada has investigated the coagulation of a number of colloidal substances by means of electrolytes. Among the substances studied by him was a colloidal solution of Copper Ferrocyanide; and he has shown that this substance is a negative colloid; and, hence coagulated by ions carrying positive charges. In conclusion he states: "The coagulating action of electrolytes on a negative colloid increases with the increase in the velocity of diffusion of the mono-valent cations = H > Cs > Rb > K > Na > Li. "(Their conduct is, in general, and holds good also for the positive colloids, proportional to the migration velocity of electrolysis and to the hydration). II." The coagulating action of electrolytes on a negative colloid increases with the increase of the electrical charge on the cation. III. In conclusion the undissociated organic substances in solution do not cause coagulation at any concentration." The Ba ions, also, were found to have very great coagulating power.

The views of Pappada are confirmed by experience gained in this laboratory in attempts to measure the osmotic pressure of solutions of Barium Chloride and Potassium Chloride.

Thus it seems justifiable to conclude—based on the results of many experiments, and by different investigators—that the membrane of Copper Ferrocyanide is of *Colloidal* nature; and that the membrane deteriorates in the presence of positive metallic ions due to the coagulation produced by the action of the positive ion on the negative colloid.

3. Gazzetta Chemica Italiana, Dec. 1911. P. 470.

(*a*) *Copper Ferrocyanide.*

That certain animal and vegetable membranes are capable of permitting the solvent to pass through, whilst hindering the passage of the solute; or, that they possess the property of semi-permeability—to some extent at least—has long been known.

Much work has been done on the various animal and vegetable membranes; but, practically no work of any value on artificial membranes, until the work of Traube[4] in 1867. Traube took up the problem of the semi-permeability of artificial membranes, and studied it, in a way, quantitatively. In the course of this work he formed many membranes, among them being Copper Ferrocyanide, and studied their semi-permeability with respect to a large number and variety of substances. The method was crude, and the results only approximations; but, never-the-less the work is of intense interest as it shows that the importance of artificial semi-permeable membranes was at that time quite fully realized, and that the necessity for accurate data on the subject of permeability was felt.

The work of Pfeffer, which is very concisely and clearly given in his "Osmotische Untersuchungeu," is, without question, the most important of the earlier work on the subject of semi-permeability and osmotic pressure. During his investigations he studied the following membranes: e'g, Copper Ferrocyanide, Parchment, Animal Tissue, Berlin-blue and Calcium Phosphate. Among the substances whose pressure he attempted to measure were; Cane Sugar, Calcium Chloride, Potassium Nitrate, Gum Arabic, Potassium Sulphate, etc. The membrane generally used by him was the Copper Ferrocyanide membrane, which he deposited by simply permitting the membrane-formers to diffuse into the wall of a porous cup. (Pfeffer appears to have been the first to realize that a porous wall, having a very close texture is a necessary prerequisite in the formation of an artificial membrane. And, unless such a finely textured wall is obtained in which to deposite and firmly root the membrane, attempts to manufacture membranes of sufficient strength to withstand high

4. Archiv f, Anatomie u, Physiologie von du Bois Reymond u, Reichert, 1867. Botan—Zeitung, 1875.

osmotic pressures, must prove unsuccessful. The other membranes mentioned above were given trials, but in every case the Copper Ferrocyanide membrane surpassed the others. In a table on page, 73 of the monograph he makes a comparison of the Copper Ferrocyanide with Parchment and Animal Tissue membranes; and in this table he demonstrates the relative adaptability of the membranes to the measurement of the osmotic pressures of solutions of Cane Sugar, Potassium Nitrate and Gum Arabic. In each case the Copper Ferrocyanide membrane was found to be superior to the others. (Further details of Pfeffer's work may be had by referring to Part, 1. of his monograph).

The next study of the Copper Ferrocyanide membranes was that made by Adie[5] during which he carried out experiments with the idea of measuring the osmotic pressure of solutions of various salts, of which the following are types; KNO_3, $NaNO_3$, KI, $CaSO_4$, $K_6Co_2C_{12}N_{13}$, and $K_2Al_2\ (SO_4)_4$, $24H_2O$; with concentrations which ranged from one fifth gram molecular weight per liter to one eightieth gram molecular weight per liter. In the deposition of the membrane he used a modified form of the method of Pfeffer; obtaining thereby a membrane of greater compactness, and by the use of which he was able to measure pressure of four and one half atmospheres.

By means of his experiments he sought to show that the various Gas Laws; e'g, The Law of Boyle, Law of Guy-Lussac, Avogadro's Hypothesis and Dalton's Law of Partial Pressures hold and can be applied to the osmotic pressure of salts in solution.

The membranes formed by the method of Pfeffer were notoriously inadequate to the accurate measurement of osmotic pressure, hence no really reliable measurements of osmotic pressure were made until 1900 when the electrolytic method for the deposition of membranes was devised in this laboratory.

The investigation[6] now in progress in this laboratory, and which is now at the close of its twelfth year, is entirely too ex-

5. Journal of the Chemical Society. 1891. p. 344.

6. Previous articles dealing with this investigation will be found in The American Chemical Journal; 26, 80; 1; 29, 137; 32, 93; 34, 1; 36, 1 and 39; 37, 324, 425 and 558; 38, 175; 39, 667; 40, 1, 194, 266 and 325; 41, 192 and 557; 45, 91, 237, 383, 517 and 654.

tensive to permit of any, but a few words in this connection. During the years of work on the problem of the osmotic pressure of solutions of Cane Sugar and Glucose, of concentrations ranging from 0.1 weight normal to 1.0 weight normal and its relation to the Laws of Boyle and Gay-Lussac the membrane in general use has been the Copper Ferrocyanide membrane. Twenty-five other membranes, formed by the electrolytic process, were studied qualitatively, more or less, but not quantitatively because of the lack of cells until recently; and many of them have shown that they possess the qualities of a good membrane; e'g, *osmotic activity, firmness, chemical inertness, insolubility* and *permanence.* The Copper Ferrocyanide membrane has given satisfactory results in the measurement of osmotic pressure for solutions of Cane Sugar of concentrations from 0.1 *weight* normal to 1.0 *weight* normal, and for temperatures ranging from 0° to 70°; and throughout the investigation this substance has maintained all the characteristics of a good membrane. The cells have only been discarded when they have become too sluggish in consequence of the extreme thickness of the membrane, to respond rapidly to slight changes of temperature and pressure, and consequently attain the maximum pressure of the solution only after a considerable length of time. The cells, when they become very slow in coming to maximum pressure and have been subject to what are known as, "Thermometer Effects" and "Barometer Effects," are discarded; but it is simply because of their slowness and not because any characteristic is wanting.

(b) *Nickel Ferrocyanide.*

During the period from the fall of 1902 to the summer of 1904, the study of twenty-six new semi-permeable membranes was made by Carver,[7] Coony,[8] and Hall,[9] in which they demonstrated their relative applicability as means of measuring osmotic pressure.

Carver in his investigation took up the study of Nickel Ferrocyanide, and has shown that, with respect to its osmotic activity it is comparable with the Copper Ferrocyanide membrane. In concluding he states: "That of the membranes studied, the re-

7. Dissertation presented, 1903.
8. Dissertation presented, 1903.
9. Dissertation presented, 1904.

sults obtained with Zinc and Nickel Ferocyanide,..... make it appear very probable that these membranes will be quite as satisfactory as the Copper Ferrocyanide membrane for measuring high osmotic pressures when suitable porous vessels are obtained in which to deposit the membrane."

Since the work of Carver the method, and details of measuring have been brought to such a state of perfection, and cells have been obtained of suitable texture for the deposition and firm rooting of the membranes. Consequently according to Carver, one should be able to obtain cells containing a membrane of Nickel Ferrocyanide, which would prove as satisfactory as those containing Copper Ferrocyanide.

With the idea in mind of testing the suitability of Nickel Ferrocyanide for the measurement of osmotic pressure, McGhee in 1910 began an investigation of this membrane in the measurement of osmotic pressure. The concentrations worked with by McGhee were 0.1 *weight* normal and 0.6 *weight* normal of Cane Sugar, and during the investigation he performed five experiments, as follows; first, 0.1 weight normal at 25° obtaining an average pressure of 2.629 atms-; gas pressure being 2.431 atms-; second, 0.1 wt N at 15° average pressure being 2.525 atms-. gas pressure 2.349 atms-; third, 0.1 wt N at 15° average pressure obtained 2.541 atms-, gas pressure being 2.349 atms-; fourth, 0.6 wt N at 30°, average pressure obtained 15.821 atms-, gas pressure being 14.830 atms-; fifth, 0.1 wt N at 30°, average pressure obtained 2.475 atms-, gas pressure being 2.472 atms-. In every case the ratio of osmotic to gas pressure lies with 0.05% of the ratio obtained with the Copper Ferrocyanide membrane. In concluding he expresses the opinion that the Nickel Ferrocyanide membrane, with respect to activity and time required to obtain a membrane of sufficient strength to withstand maximum pressure, surpasses the membrane of Copper Ferrocyanide.

OBJECT.

In a recent paper by Prof. Morse[10] the following statement appears: e'g, "It was found long ago that a considerable number of osmotically active membranes could be readily produced by the electrolytic method; but though twenty-five of these have been

10. American Chemical Journal: Vol. XLV. 557.

made and tested qualitatively, we could not, until recently, spare the cells for the purpose of testing their suitability for quantitative work. The Ferrocyanide of Nickel appears to be superior in some respects to the corresponding salt of Copper, but a comparison of the two will be withheld until a more thorough study of the former has been made."

The general use of the Copper Ferrocyanide membrane, until two years ago, was necessitated—as spoken of above—by a lack of good cells, which, also, prevented the study of other membranes as a means of measuring osmotic pressure. However during the past year a sufficient number of cells came to hand to make possible a direct comparison of the Nickel and Copper Ferrocyanide membranes. Consequntly, the present investigation was undertaken with the purpose of determining the comparative adaptability of the two membranes in the measurement of osmotic pressure, with special attention to their comparative *firmness, chemical inertness, osmotic activity, insolubility* and *permanence.*

THE CELLS.

The cells used in the following work were manufactured according to the method[11] in general use in this laboratory, with a slight modification in the manner of firing and forming the cylinders.

Previously the cells were heated in the kiln to a temperature, not exactly known, but probably in the neighborhood of the fusion point of seger cone, 7, and they were subjected to one firing. The latest cells were fired at a higher temperature, the 9th seger cone, or in the vicinity thereof and the firing was repeated. This method of procedure was desirable and chosen in order to make texture of cell wall more compact. The texture of the cell wall must be extremely fine in order to provide a suitable support for the membrane. It was thought that this result would be obtained by taking advantage of the greater shrinkage caused by the higher temperature and repeated firing; since the greater the shrinkage the finer will the pores of the cell wall become.

11. American Chemical Journal: Vol. XLV. 91.

Another modification in the method of cell preparation should not be passed without a few words in regard to it. The press in which the clay is tightly compressed into the form of a cylinder causes the contraction to take place in only one direction; e'g. vertically, due to the interior of the press being truly cylindrical. In these cells, after being shaped on the lathe, it was noticed that portions exhibited a wavy appearance, which it was thought might be caused by non-uniform contraction when the cylinder was being pressed. In order to obviate this non-uniformity a shell, tapered internally, was made which fits into the press and by which a lateral as well as a vertical contraction is brought about. Thus far only one cell has been so produced. This cell after being shaped showed only a very slight wavy appearance, but on firing a crack was produced at the top of sufficient size to so weaken the structure that on being set-up the second time the cell broke under the mechanical pressure being applied. Consequently, as to whether the clay pressed cylindrically or conically is better adapted for the manufacture of cells remains a question to be solved by future investigation.

The cells used in this work are known as; T_6, N_6, K_6, F_6, Y_6, Z_6, C_6, S_6, B_6, G_6, O_6, L_6, Q_6, and H_6. The cells T_6, N_6, K_6, F_6, Y_6, Z_6, C_6, were used for the deposition of Copper Ferrocyanide, and in cells S_6, B_6, G_6, O_6, L_6, Q_6, and H_6, Nickel Ferrocyanide was deposited.

All the cells were produced under exactly the same conditions to render the comparison more complete.

PREPARATION OF MEMBRANE.

(a) *Removal of Air.*

The method used in this laboratory for the removal of air from the cell wall is by the electrolysis of a 0.005 ion normal solution of Li_2SO_4. Under the influence of the electric current the Li ions, which are largely hydrated, sweep through the pores of the cell wall, and as a consequence remove all the air.

At this stage, and, also, during the subsequent removal of the electrolyte by means of pure water, an idea as to the density of the cell wall may be obtained by observing the amount of liquid delivered by electric osmose, during the period of subjection to the influence of the current.

A careful record of the liquid delivered was kept, and the densities, of the walls of the various cells, were found to compare according to the following scheme: $Q_6 > C_6 > T_6 > N_6 > Y_6 > Z_6 = K_6 = F_6 = S_6 = B_6 = G_6 = O_6 = L_6 = H_6$.

(b) Deposition of the Membranes. [12]

The membranes were deposited according to the method referred to above. The distribution of cells was according to that stated under section; The Cells.

In the case of Copper Ferrocyanide deposition the membrane-formers were 0.1 *volume normal*—one tenth of a gram molecular weight dissolved and diluted to the volume of one liter at 20°—$CuSO_4$, and 0.1 *volume normal* $K_4Fe(CN)_6$; the electrodes being sheet Copper in the outer vessel, constituting the anode, and Platinum within the cell, constituting the Cathode. For the deposition of Nickel Ferrocyanide, 0.1 *volume normal* $NiSO_4$ and 0.1 *volume normal* $K_4Fe(CN)_6$ were the membrane formers; sheet Nickel being the Anode and Platinum serving as the Cathode.

Unfortunately a short time before the deposition began the storage battery, which served as the source of supply of the electricity used for the membrane deposition had to be removed from service. This removal, which was caused by a marked deterioration of the individual storage cells, and, consequently, a great decrease in the efficiency of the battery, necessitated placing the deposition line on the 115 volt main of the city. This change would not have proven disadvantageous had it not been that the voltage was shown to be too high.

After the cells had been subjected to the membrane-forming process a second time under the influence of the 115 volt main; and were being removed from the deposition bath, washed and placed in a saturated solution of Thymol, a deposit was observed on the outer wall of the cells. This deposit was more marked in the case of the Copper Cells than with the Nickel Cells. (The terms Copper Cells and Nickel Cells designate cells containing a membrane of $Cu_2Fe(CN)_6$ and a membrane of $Ni_2Fe(CN)_6$

12. For further details regarding the methods of manufacture of the cells, removal of air, and deposition of the membranes reference should be made to the recent articles; American Chemical Journal; Vol. XLV. 91, 521, 522.

respectively). A deposit of any nature what-so-ever, on the outer wall of a cell is to be entirely avoided, if possible. From previous work it was at once realized that the cause, of the formation of the deposit, was an excessive voltage on the deposition line. In order to eliminate this objectionable feature, an arrangement for controlling the voltage was devised and installed. This arrangement may be briefly described as follows: the current from the positive side of the circuit is first lead into a cut-out block containing a 16 candle power 110 volt lamp, from which it passes, in series, through an adjustable rheostat, and finally back to the opposite side of the circuit. The membrane-forming line or circuit, was then connected in parallel, with the lamp, and by adjustment of the rheostat a range of voltage from 102 to 113 volts can be obtained. The device, above described, gave the improvement anticipated, and by operating at 106 volts the deposits ceased to occur, and gradually diminished in area as the cells were repeatedly subjected to the depositing process.

On examining the outside solutions used in membrane deposition; i'e, $CuSO_4$ or $NiSO_4$ according to the membrane, there was observed to be—in the copper solution, a considerable contamination which rendered the solution unfit for further use. This contamination, however, did not occur in the nickel solution. As the solutions are made up with a saturated solution of Thymol, it was thought at first, that the Thymol had in some way produced the noticed effect. To test this; solutions were used, which had been made up with distilled water, but the same contamination resulted. Taking into consideration the fact that the nickel solutions are not so effected, and, also, that copper solutions are more easily reduced under the influence of the electric current than nickel solutions, it seems very probable that th contamination is a result of the formation of *CuS* due to the reduction of $CuSO_4$. This becomes, quite evident, when reference is made to the electrode tensions necessary to deposit copper and nickel from solutions of their sulphates. The tension necessary to reduce copper being 2.5 to 3.2 volts, and for nickel 3.1 to 3.8 volts with a current density of 0.5 ampere in the case of copper and 1.0 ampere for nickel. The complete elimination of the reducing effect of the current can not be realized, as the current necessary for a satisfactory membrane deposition easily reduces the $CuSO_4$. However, by frequent renewals—at alternate

runnings—the $CuSO_4$ solution can be maintained in a sufficiently uncontaminated condition to give results wholly satisfactory. That this reducing action is also felt by the membrane will be brought out later.

As has been stated in previous contributions[13] a quite frequent renewal of the Potassium Ferrocyanide solution is necessitated because of the accumulation of caustic alkalie, which has a deleterious action upon the membranes. That a marked decrease in the resistance, or increase in the current takes place during the interval of time that the new solution is entering by the funnel-tube and the old solution passing out by the delivery-tube, was observed; and the following explanation suggested; "When the liquid has ceased to flow from the cells, after a pouring, the current invariably decreases till it becomes the same that it was before the change of solution, so that the cause can not be in the difference of the two solutions. It is possible that the force of the flowing liquid produces a mechanical disturbance which reduces the resistance for the time." In considering this current increase the observation was made that the current increases to a maximum at once when the outflowing solution touches the metal trough, which serves to carry the old solution away from the bath, and diminishes to its original value immediately when the flow ceases. The effect produced when the outflow is received in a glass receptacle, was tested, and it was found that no increase in the value of the current takes place. Also when the liquid flowing from the delivery-tube flows in drops and not continuously, there is no increase in the current. From these observations the explanation which suggests itself is quite simple. When the solution leaving the cell touches the metal trough, electrical contact is made and as a consequenc, a less resistant path is offered to the current. The current, immediately, flows along the less resistant path, increases to a maximum and remains there till the outflow ceases. The contact then being broken, the current returns to its former value. This explanation, though extremely simple, is in direct accord with the facts, and the construction to be applied to them.

CONSTANT TEMPERATURE BATHS.

The constant temperature baths in this laboratory are of two

13. See note 6, p. 8.

types; e'g, the rectangular, or wooden, copperlined, and the circular or brass baths. The bath in which the cells were placed for comparison was of the rectangular type. The baths and the system of temperature control have been previously described,[14] therefore only two changes made during the year will be touched upon.

Here-to-fore the temperature control consisted of a relay two condensers, stoves—electrical—, thermostat, a single battery cell and two lamps. The condensers and lamps were so arranged as to eliminate sparking, to a great extent, between the platinum points of the relay, and the mercury and platinum wire of the thermostat. This system whilst giving almost perfect temperature control, was faulty in that it did not wholly eliminate sparking in the relay and thermostat: thus in the former causing the points to stick, and in the latter contaminating the mercury to such a degree that long continued exact regulation became difficult. These difficulties have been entirely overcome, by Prof. Morse, by the installation of a new temperature control system.

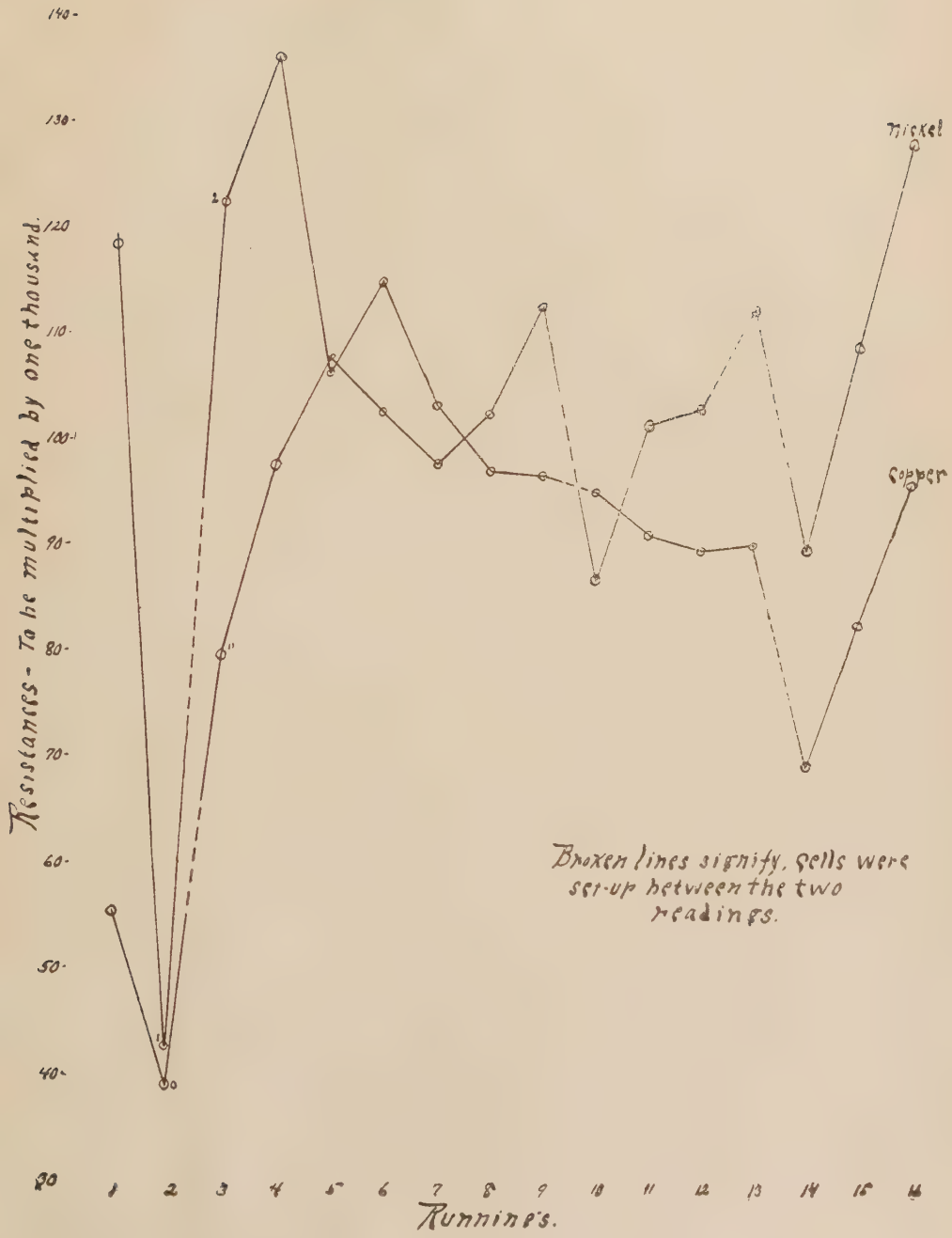
The new system is similar to the older one, except for the introduction of a master-relay of high resistance, which is controlled by the thermostat, the elimination of the old condenser method for obviating sparking, and, also, each stove has its own relay of smaller resistance controlled by the master-relay. No other current except that going through the single master-relay being necessary for the accurate working of the system, and the spark-gaps of the thermostat and relay being spanned by high resistance lamps, the current is decreased—never broken—to such an extent that no visible sparking is produced. The sparking in the relays—stove—is eliminated by spanning the spark-gaps with high resistance lamps which, when the stove circuit is broken, permit a small amount of current to flow continuously. Thus the current flowing in the stove circuit is not broken abruptly, but it is simply reduced to a very small value.

Briefly stated. Sparking in the thermostat has been eliminated by the introduction of a high resistance relay, and by spanning the spark-gaps with high resistance lamps. From the stove relays it has been done away with by diminishing the stoves—lamps—from 16 candle power to 8 candle power wherever practi-

14. American Chemical Journal; Vol. XLV. 383.

Plate I

Resistances



cable to do so, and by having the spark-gaps spanned by lamps of high resistance.

Accordingly it will be observed from the foregoing, that the two objections to the old system have been entirely overcome; and that the present system, although simpler, is much more efficient.

The second change has to do with the make up of the interior of the bath. In the arrangement previously in vogue the cells when placed in the bath, were received into six cans which were held in place by having heavy lead weights fastened to the bottom of each can. The later arrangement consists of two long troughs 830 mm long, 150 mm wide and 410 mm high, surrounded by water in the lower part of the bath. The present division of space enables one to place a maximum of forty cells in the bath, whereas in the case of the older distribution only six cells could be placed for measurement. An objection, which arose to the present distribution; e'g, that it would be difficult to maintain the cells at the temperature of the water in the bath because of the greatly enlarged air space, has been surmounted by filling up the spaces between the bottles, containing the cells, and a portion of the trough above with lambs wool. This arrangement has been the means of greatly facilitating the work during the past year. Without it, undoubtedly, not more than one half of the work accomplished could have been carried out, on account of lack of space.

COMPARISON OF RESISTANCE.

The comparison of the resistances of cells containing on the one hand a membrane of Copper Ferrocyanide and on the other a membrane of Nickel Ferrocyanide was carried out whilst the membranes were being deposited in the cells, in preparation for setting-up with a solution of cane sugar of 0.5 weight normal concentration. The voltage was maintained at a constant value —excepting the first two runnings—by means of the constant voltage arrangement already noted; and the current read by means of a weston millammeter, which could be connected with each individual cell, and disconnected readily by a system of hubbell-plugs. The voltage during the first and second runnings was 115 volts, which—as already stated—was found to be excessive, and there-after it was kept constant at 106 volts. The cells

were subjected to the membrane-forming process for one hour each day. After each running the cells were placed in large desicators containing a saturated solution of Thymol, and allowed to soak until subsequently subjected to the membrane-forming process. The effect of the soaking being, that it removes the electrolyte in contact with the membrane, and there-by overcomes its deleterious action.

The use of a saturated solution of Thymol is necessitated by an infection of the laboratory by the fungus *Penicillium glaucum,* which attacks the membranes and quickly ruins them, the Thymol destroys the growth and does not harm the membranes.

At the end of each days running the current passing through the membrane was measured, and the resistance calculated.

In tables, I and III, VII and IX, XIII and XV, following, are given the resistances of the various cells at the end of each days running. Tables, I, VII and XIII giving the values for the copper cells, and tables, III, IX and XV giving the values for the nickel cells.

Column D: Date on which cells were run.

Columns designated as T_6, N_6, K_6, etc., in tables I, VII, and XIII give the values of resistance for the individual copper cells.

Columns designated as S_6,B_6, G_6, etc., in tables III, IX and XV give the resistance values for the individual nickel cells.

The experiments—data of which are given in tables, II and IV, VIII and X, XIV and XVI following—demonstrating the conduct of the membranes in the development and maintenance of pressure, were carried out with solutions of Cane Sugar of 0.5 weight normal concentration.

Solutions of 0.5 weight normal concentration were used, as previous investigation had shown that the 0.5 weight normal solutions are more suitable for the development of new membranes than solutions of smaller concentration.

During the first setting-up of the new cells a record of the respective pressures was not kept; as the object was simply to "season" the membranes by subjecting them to pressure, and thus rendering them more compact.

The solutions of which attempts were made to measure the osmotic pressures were made up 0.01 *osmotically* normal with respect to potassium ferrocyanide, the salt being considered as

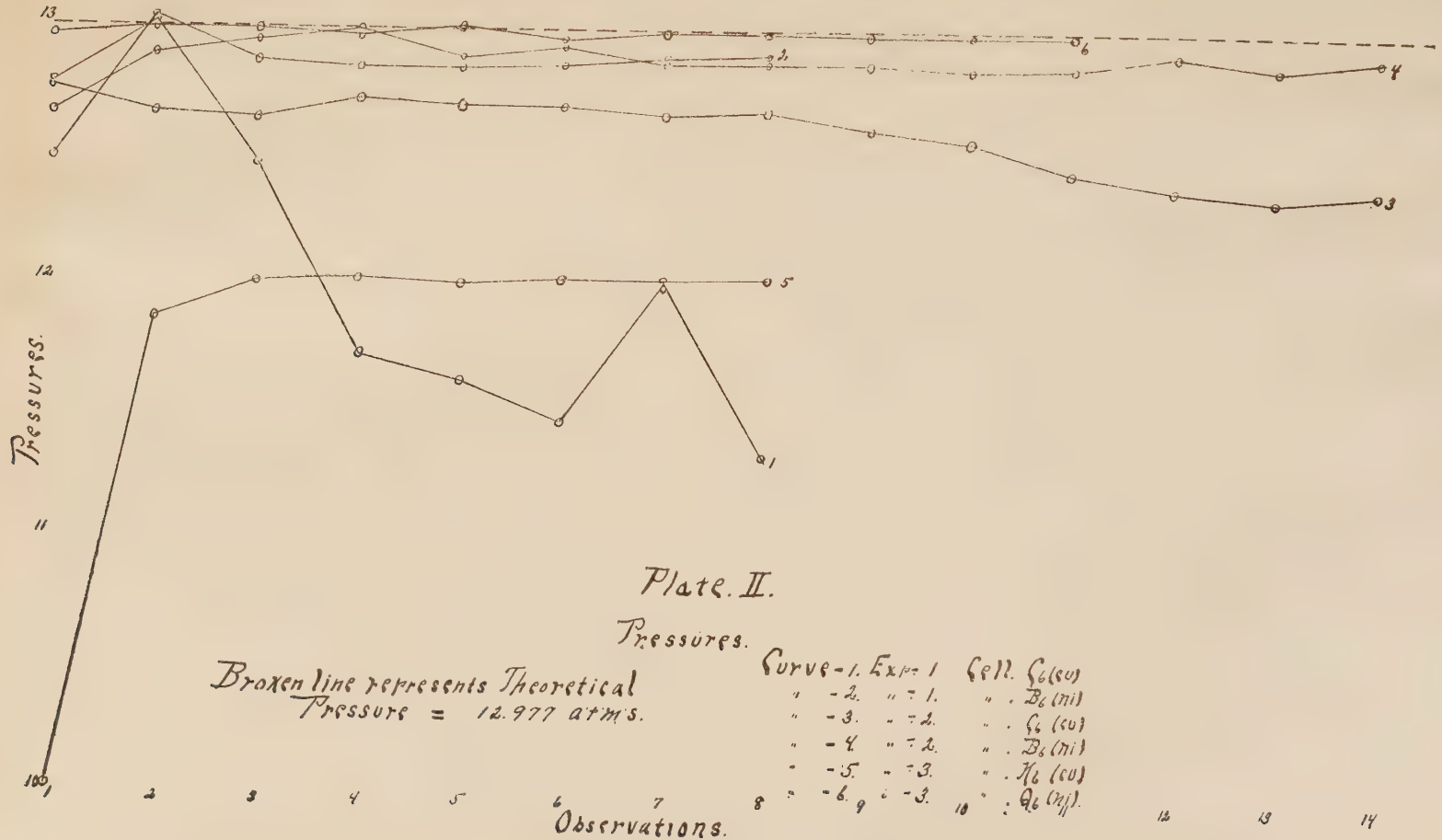


Plate. II.

Pressures.

Broken line represents Theoretical Pressure = 12.977 atm's.

Curve-1. Exp= 1 Cell. C_6(cu)
" -2. " = 1. " . B_6(ni)
" -3. " = 2. " . C_4 (cu)
" -4 " = 2. " . B_8(ni)
" -5. " = 3. " . H_6 (cu)
" -6. " = 3. " : Q_6 (ni).

completely dissociated at that dilution. The exact quantity of the salt dissolved in 100 gram of water being 83.9 milligrams. The solutions were, also, made 0.001 normal with respect to thymol, the purpose being that already stated.

The water in which the cells are placed for measurement is made up 0.01 *osmotically* normal with respect to copper sulphate, in case of the Copper Ferrocyanide membrane; and 0.01 *osmotically* normal with respect to nickel sulphate, in the case of the Nickel Ferrocyanide membrane. The solutions are, also, made 0.001 normal with respect to thymol.

The purpose of the potassium ferrocyanide and copper sulphate, or potassium ferrocyanide and nickel sulphate—as the case may be—in the solution, being to mend and rent, or rents that may occur in the membrane whilst the cell is up for measurement.

The method followed in setting-up the cells, the manner of reading the manometers, etc., may be obtained by referring to the articles named in the foot-note on page 18.

EXPERIMENT 1.

TABLE I.

Resistances. $(Cu_2Fe(CN)_6)$.

D	T_6	N_6	K_6	F_6
Mar. 21,	275.000	137.500	91.660	110.000
Mar. 22,	87.690	50.000	20.540	32.810
Mar. 27,	157.140	157.140	110.000	110.000
Mar. 28,	214.000	152.850	107.000	118.890
Mar. 29,	.....	120.000	108.000	108.000
Mar. 30,	.....	145.000	118.890	118.890
Apr. 1,	145.000	107.000	107.000	97.270
Apr. 2,	118.890	107.000	107.000	82.300
Apr. 3,	118.890	107.000	107.000	89.160

D	Y_6	Z_6	C_6
Mar. 21,	84.610	42.310	55.000
Mar. 22,	32.860	15.970	60.350
Mar. 27,	110.000	91.660	122.220
Mar. 28,	107.000	107.000	152.850
Mar. 29,	108.000	90.000	.....
Mar. 30.	97.270	97.270	.....
Apr. 1,	89.160	62.950	118.890
Apr. 2,	76.240	72.000	118.890
Apr. 3,	82.300	82.300	118.890

Cells set-up for "seasoning" between Mar. 22 and Mar. 27.

TABLE II.

Pressures. $(Cu_2Fe(CN)_6)$

Column D: Date of observation.

Column T: Time of taking observation.

Column N_6, K_6, Y_6, etc., osmotic pressures developed and maintained in the respective cells.

D	T	N_6	K_6	Y_6	Z_6	C_6
Apr. 3,	8 P. M.	13.018	7.203	11.611	11.694	12.757
Apr. 4.	10 A. M.	11.131	6.582	11.426	11.626	13.012
Apr. 5.	10 A. M.	9.916	6.830	11.539	11.964	12.472
Apr. 6.	10 A. M.	.....	6.931	11.554	12.049	11.743
Apr. 7.	4 P. M.	.....	6.870	10.873	12.110	11.628
Apr. 8.	8 P. M.	.....	6.725	11.180	12.084	11.460
Apr. 9.	8 P. M.	.....	6.689	11.272	12.058	12.012
Apr. 10.	3 P. M.	.....	.....	11.376	12.094	11.338

Time of setting-up, April 3. 4 P. M.

Solution: 0.5 weight normal Cane Sugar.

Theoretical gas pressure, 12.358 atm-.

Temperature of experiment, 30°.

True osmotic pressure, 12.977 atms-.

TABLE III.

Resistances. $(Ni_2Fe(CN)_6)$

D	S_6	B_6	G_6	O_6
Mar. 21.	55.000	55.000	57.890	78.570
Mar. 22.	31.060	43.820	46.000	76.660
Mar. 27.	73.330	78.570	78.570	110.000
Mar. 28.	76.360	110.000	106.000	117.780
Mar. 29.	108.000	108.000	.....	.....
Mar. 30.	97.270	107.000	.....	.....
Apr. 1.	118.890	107.000	72.000	107.000
Apr. 2.	107.000	107.000	97.270	107.000
Apr. 3.	107.000	118.890	107.000	152.850

D	L_6	Q_6	H_6
Mar. 21.	36.660	55.000	55.000
Mar, 22.	23.000	31.060	28.750
Mar. 27.	57.890	84.610	78.570
Mar. 28.	88.330	106.000	88.330
Mar. 29.	108.000	108.000	108.000
Mar. 30.	97.270	107.000	107.000
Apr. 1.	89.160	97.270	97.270
Apr. 2.	89.160	107.000	107.000
Apr. 3.	82.300	118.890	107.000

Cells set-up for "seasoning" between Mar. 22 and Mar. 27.

TABLE IV.

Pressures $(Ni_2Fe(CN)_6)$

Column D: Date of observation.

Column T: Time of taking observation.

Columns, S_6, B_6, O_6, etc., osmotic pressures developed and maintained in the respective cells.

D	T	S_6	B_6	O_6	L_6	Q_6
Apr. 3.	8 P. M.	10.474	12.866	12.475	12.196	10.756
Apr. 4.	10 A. M.	10.844	13.050	12.626	12.395	11.192
Apr. 5.	10 A. M.	10.684	12.863	12.661	12.478	11.157
Apr. 6.	10 A. M.	10.598	12.842	12.650	12.453	11.007
Apr. 7.	4 P. M.	15.540	12.842	12.620	12.476	10.873
Apr. 8.	8 P. M.	10.499	12.854	12.633	12.497	10.873
Apr. 9.	8 P. M.	10.479	12.870	12.655	12.481	10.868
Apr. 10.	3 P. M.	10.482	12.893	12.628	12.565	10.815

Time of setting-up, April 3. 4 P. M.
Solution: 0.5 weight normal Cane Sugar.
Theoretical gas pressure, 12.358 atms-.
Temperature of experiment, 30°.
True osmotic pressure, 12.977 atms-.

TABLE V.

Column A.Pcu. Daily average of pressures observed in the copper cells.

Column A.Pni. Daily average of pressures observed in the nickel cells.

Column R,cu. Daily average of resistance observed in the copper cells.

Column R,ni. Daily average of resistance observed in the nickel cells.

A.Pcu	A.Pni	R.cu.	R.ni.
11.256_1	11.753_1	113.750	56.160
10.755_1	12.021_1	43.106	39.317
10.544_1	11.969_1	122.580	80.193
10.567_2	11.910_1	137.084	98.400
10.370_2	11.858_1	106.000	110.000
10.362_2	11.871_1	112.494	103.108
10.508_2	11.870_1	97.394	103.070
11.602_3	11.876_1	97.263	113.418

Sub-numerals 1, 2 and 3 designate an average of five, four and three cells respectively.

TABLE VI.

Time of setting-up, April 3. 4 P. M.

Column M: Time, in hours, necessary for the copper cells to develop to their maximum.

Column P: Time, in hours, necessary for the nickel cells to develop to their maximum.

Copper Cells.	M.	Nickel Cells.	P.
N_6	4	S_6	18
K_6	4	B_6	18
Y_6	4	O_6	42
Z_6	90	L_6	18
C_6	18	Q_6	18

EXPERIMENT 2.

TABLE VII.

Resistances. $(Cu_2Fe(CN)_6)$.

D	T_6	N_6	K_6	F_6
Apr. 11.	117780	81530	81530	66250
Apr. 12.	117780	96360	88350	66250
Apr. 13.	117780	96360	66250	62350
Apr. 14.	117780	106000	55790	70660

D	Y_6	Z_6	C_6
Apr. 11.	75710	81530	106000
Apr. 12.	66250	88250	117780
Apr. 13.	96360	88350	106000
Apr. 14.	117780	88350	106000

TABLE VIII.

Resistances. $(Cu_2Fe(CN)_6)$.

Column D: Date of observation.

Column T: Time of taking observation.

Columns C_6, T_6, F_6, etc., osmotic pressures developed and maintained in the respective cells.

D	T	C_6	T_6	F_6
Apr. 15.	.....	12.749_1	15.697_1	12.480_1
Apr. 16.	.....	12.646_1	14.066_1	12.025_1
Apr. 17.	3 P. M.	12.627	13.378	12.540
Apr. 18.	4 P. M.	12.712	12.936	12.586
Apr. 19.	.....	12.698_1	12.857_1	12.114_1
Apr. 20.	3 P. M.	12.689	12.840	12.697
Apr. 21.	4 P. M.	12.658	12.859	12.705
Apr. 22.	.....	12.667_1	12.873_1	12.778_1
Apr. 23.	9 A. M.	12.605	12.769	12.752
Apr. 24.	.....	12.561_1	12.864_1	12.765_1
Apr. 26.	.....	12.440_1	13.153_1	12.834_1
Apr. 27.	.....	12.371_1	13.178_1	12.831_1
Apr. 28.	8 P. M.	12.344	13.210	12.853
Apr. 29.	3 P. M.	12.372	13.272	12.907

D	T	Y_6	N_6	Z_6	K_6
Apr. 15.	.....	13.076_1	12.787_1	12.309_1	8.358_1
Apr. 16.	.....	12.076_1	10.905_1	11.623_1	10.324_1
Apr. 17.	2 P. M.	12.174	.....	11.502	10.624
Apr. 18.	4 P. M.	12.453	.....	11.664	10.784
Apr. 19.	.....	12.560_1	.....	11.814_1	10.841_1
Apr. 20.	3 P. M.	12.661	.....	11.924	10.891
Apr. 21.	4 P. M.	12.437	.....	11.871	10.895
Apr. 22.	.....	12.552	.....	11.899	10.915

$_1$ designates mean of days observations.

TABLE IX.

Resistances. $(Ni_2Fe(CN)_6)$

D	S_6	B_6	G_6	O_6
Apr. 11.	70660	81530	106000	106000
Apr. 12.	96360	106000	106000	117780
Apr. 13.	106000	117780	117780	132500
Apr. 14.	106000	117780	117780	132500

D	$L_6(_2)$	Q_6	H_6
Apr. 11.	58890	96360	88250
Apr. 12.	75710	106000	105000
Apr. 13.	96360	117780	106000
Apr. 14.	106000	106000	106000

$(_2)$ Cell L_6 was broken, whilst being set-up in this experiment, due to a crack which was produced during firing.

TABLE X.

Resistances. $(Ni_2Fe(CN)_6)$

Column D: Date of observation.

Column T: Time of taking observation.

Columns O_6, B_6, G_6, etc., osmotic pressures developed and maintained in the respective cells.

D	T	O_6	B_6	G_6	Q_6	S_6
Apr. 15.	.....	13.866_1	12.645_1	12.582_1	10.814_1	11.102_1
Apr. 16.	.....	13.211_1	12.866_1	12.083_1	12.509_1	12.146_1
Apr. 17.	3 P. M.	13.189	12.944	11.971	12.537	12.028
Apr. 18.	4 P. M.	12.235	12.981	11.966	12.547	11.928
Apr. 19.	.....	13.151_1	12.184_1	11.949_1	12.554_1	11.941_1
Apr. 20.	3 P. M.	13.168	12.846	12.007	12.546	11.946
Apr. 21.	4 P. M.	13.138	12.864	12.033	12.558	11.923
Apr. 22.	.....	13.162_1	12.860_1	12.054	12.555	11.927
Apr. 23.	9 A. M.	13.147	12.863			
Apr. 24.	.....	13.139	12.837			
Apr. 26.	.....	13.128_1	12.854_1			
Apr. 27.	.....	13.095_1	12.889_1			
Apr. 28.	8 P. M.	13.130	12.854			
Apr. 29.	3 P. M.	13.114	12.889			

$_1$ designates mean of days observations.

Cells G_6, Q_6, and S_6 were taken down on Apr. 22 as their conduct had shown that they would not develop the true pressure of the solution.

Time of setting-up, April 15, 11 A. M.

Solution: 0.5 weight normal Cane Sugar.

Theoretical gas pressure, 12.358 atms-.

Temperature of the experiment, 30°.

True osmotic pressure, 12,977 atms-.

TABLE XI.

Column A.Pcu. Daily average of pressures observed in the copper cells.

Column A.Pni. Daily average of pressures observed in the nickel cells.

Column R.cu. Daily average of resistances observed in the copper cells.

Column R.ni. Daily average of resistances observed in the nickel cells.

A.Pcu	A.Pni	R.cu.	R.ni.
12.494_7	12.202_5	95761	86829
11.952_6	12.563_5	91589	101978
12.141_6	12.534_5	90207	103459
12.189_6	12.531_5	90418	113151
12.144_6	12.496_5		
12.284_6	12.520_5		
12.242_6	12.503_5		
12.276_6	12.512_5		
12.730_3	13.004_2		
12.809_3	12.978_2		
12.793_3	12.991_2		
12.802_3	12.992_2		
12.850_3	12.992_2		
	13.031_2		

The sub-numerals signify the number of cells, whose pressures were averaged.

TABLE XII.

Time of setting-up, April 15. 11 A. M.

Column M: Time, in hours, necessary for the copper cells to develop their maximum.

Column P: Time, in hours, necessary for the nickel cells to develop their maximum.

Copper Cells.	M.	Nickel Cells.	P.
C_6	5.5	O_6	....
T_6	5.5	B_6	51.5
F_6	...	G_6	....
Y_6	5.5	Q_6	90.0
N_6	5.5	S_6	18.0
Z_6	5.5		
K_6	...		

Cells F_6 and K_6 did not give any well defined maximum, but gradually rose to the final.

Cells O_6 and G_6 the initial pressure exceeded the true pressure of the solution.

EXPERIMENT 3.

TABLE XIII.

Resistances. ($Cu_2Fe(CN)_6$).

D	N_6	K_6	Y_6	Z_6
Apr. 23.	96360	55790	70660	55790
Apr. 24.	106000	62350	88350	75710
Apr. 25.	117780	81530	96360	38350

TABLE XIV.

Resistances. ($Cu_2Fe(CN)_6$).

Column D: Date of observation.

Column T: Time of taking observation.

Columns N_6, K_6, etc., osmotic pressures developed and maintained in the individual cells.

D	T	N_6	K_6	Z_6	Y_6
Apr. 25.	12 N.	11.405	5.496	.....	9.464
Apr. 26.	9 A. M.	11.872_1	10.144_1	9.894_1	15.006_1
Apr. 27.	.....	10.529_1	11.861_1	10.880_1	14.949_1
Apr. 28.	8 P. M.	.....	12.014	11.534	14.849
Apr. 29.	3 P. M.	.....	12.104	11.708	14.879
Apr. 30.	9 A. M.	.....	12 040	11.773	10.073
May. 1.	.....	$.....{}_1$	12.064_1	11.824_1	10.205_1
May. 2.	.....	$.....{}_1$	12.074_1	11.793_1	10.406_1
May. 3.	9 A. M.	.....	12.061	11.880	

($_1$) designates mean days observations.

TABLE XV.

Resistances. ($Ni_2Fe(CN)_6$)

D	S_6	G_6	Q_6	H_6
Apr. 23.	75710	81530	96360	106000
Apr. 24.	96360	106000	117780	117780
Apr 25.	117780	106000	132500	132500

TABLE XVI.

Pressures. $(Ni_2Fe(CN)_6)$

Column D: Date of observation.

Column T: Time of taking observation.

Columns S_6, G_6, Q_6 osmotic pressures developed and maintained in the individual cells.

D	T	S_6	Q_6	G_6
Apr. 25.	12 N.	8.108	8.702	13.022
Apr. 26.	.....	12.649_1	12.948_1	7.878_1
Apr. 27.	.....	12.981_1	12.981_1	8.076_1
Apr. 28.	8 P. M.	12.603	12.983	7.975
Apr. 29.	3 P. M.	12.607	12.970	8.055
Apr. 30.	9 A. M.	12.542	13.022	.....
May. 1.	.....	12.535_1	12.952_1	.....
May. 2.	.....	12.532_1	12.968_1	.....
May. 3.	9 A. M.	12.539	12.978	.....
May. 4.	.....	12.539_1	12.973_1	.....
May. 5.	.....	12.568	12.970	.....
May. 6.	9 A. M.	12.569	12.973	.....

$(_1)$ designates mean of days observations.

Time of setting-up, April 25. 12 noon.

Solution: 0.5 weight normal Cane Sugar.

Theoretical gas pressure, 12.358 atms-.

Temperature of the experiment, 30°.

True osmotic pressure, 12.977 atms-.

TABLE XVII.

Column A.Pcu. Daily average of pressures observed in the copper cells.

Column A.Pni. Daily average of pressures observed in the nickel cells.

Column R.cu. Daily average of resistances observed in the copper cells.

Column R.ni. Daily average of resistances observed in the nickel cells.

A.Pcu	A.Pni	R,cu.	R,ni
8.788_4	9.944_3	69650_4	89900_4
11.979_4	11.140_3	93102_4	109480_4
12.055_4	11.312_3	96005_4	128820_4
12.466_3	11.220_3		
12.563_3	11.211_3		
11.295_3	12.782_2		
11.364_3	12.743_2		
11.485_3	12.755_2		
11.971_2	12.755_2		
	12.755_2		
	12.769_2		
	12.771_2		

Sub-numerals designate number of cells averaged.

TABLE XVIII.

Time of setting up, April, 25. 12 noon.

Column, M: Time, in hours, necessary for the copper cells to develop their maximum.

Column, P: Time, in hours, necessary for the nickel cells to develop their maximum.

Copper Cells.	M.	Nickel Cells.	P.
N_6	21	S_6	21
K_6	99	Q_6	21
Z_6	..	G_6	..
Y_6	32		

Cell Z_6 did not give a well defined maximum, but gradually rose to the final pressure.

Cell G_6, the initial pressure exceeded the true osmotic pressure.

DISCUSSION OF DATA.

At the beginning of the membrane-forming process, the resistances of the individual copper cells exceeded, very markedly, those of the individual nickel cells, but as the cells were repeatedly subjected to the deposition process the resistance of the nickel cells gradually rose until it surpassed that of the copper cells. Having surpassed the copper cells with respect to resistance, the nickel cells have continued to maintain the high resistance, and to increase it on subsequent repetitions of the membrane-forming process; whereas the copper cells have, practically, remained at the same value. The maximum resistance of the copper cells being, approximately, 100,000 ohms, whilst the resistance in the nickel cells reached a value of 132,000 ohms. The higher resistance in the cells containing a membrane of Nickel Ferrocyanide may, possibly, be due to the colloidal condition of the Nickel Ferrocyanide being less effected by the action of the electrolytes.

That the newly formed membrane must be subjected to pressure after a few days running, in order to render it more compact; and that the "seasoning" process is a necessary procedure in the preparation of a new membrane may be readily seen on examining the data given under Table V. The cells were set-up for "seasoning" between March 22 and 27; and the resistance calculated after the first running subsequent to "seasoning" showed an increase of 150% in the case of the copper cells and 100% in the nickel cells. This effect is, also, very clearly shown by the curves represented in Plate I. The points 1 and 2, and o and ″ on the curves for Copper Ferrocyanide and Nickel Ferrocyanide, respectively, represent, graphically, the resistances immediately preceding the "seasoning" and immediately afterward. The points 1 and o giving the value prior, and points 2 and ″ subsequent to "seasoning."

A further examination of the results—tabular and graphic—shows that the membranes after being set-up with a solution of Cane Sugar for several days, are of a much lower resistance—until repeatedly subjected to the deposition process—than before they were placed in the presence of the solution. This effect is very evident in the case of both membranes. It, however, is

slightly more marked in the case of the Nickel than of the Copper Ferrocyanide membrane.

Tables II, VIII and XIV, and IV, X and XVI, and the curves in Plate II present the conduct of the membranes whilst under pressure. Tables II, XIV and VIII, and IV, X and XVI giving the results obtained with Copper Ferrocyanide and Nickel Ferrocyanide, respectively.

An examination of the numerical data, and a reference to the graphical representation of the results obtained with typical cells, reveals the fact that the pressures developed and maintained by the Nickel Ferrocyanide membrane are markedly higher, and more nearly the true osmotic pressure than that developed and maintained by the membrane of Copper Ferrocyanide. Also, that the pressures developed in the nickel cells do not fluctuate from day to day, but having developed a certain pressure that pressure is maintained constant: whereas in the case of the copper cells the pressures do fluctuate, and not until the membrane has become quite thick will a pressure be maintained at a constant value. The presence of fluctuations in the conduct of the copper cells and the absence thereof in the cases of the nickel cells makes it evident that the membrane of Nickel Ferrocyanide is more permanent, and of greater firmness under the influence of pressure than the Copper Ferrocyanide membrane.

With regard to the relative activities of the membranes the results tabulated under tables, VI, XII, and XVIII exhibit, that the time necessary for the Copper Ferrocyanide membrane to develop the maximum pressure is less than that required for the Nickel Ferrocyanide; whilst the membranes are in the preparatory condition. But as the membranes become of sufficient strength to measure the pressures developed by the solutions, the activities become—practically speaking—of the same order of magnitude. Thus it is shown that, although the activity of the Copper Ferrocyanide membrane is slightly greater than the activity of the membrane of Nickel Ferrocyanide, during the early stages of membrane formation, never-the-less when the membranes have been developed to the measuring point their activities are relatively equal.

The pressures observed during the investigation are in direct accord with, and confirmed by the results obtained previously in this laboratory.

The results, also, demonstrate that the nickel cells develop and maintain, in a shorter time, more nearly the true pressure of the solution; and that—with identically the same treatment while, probably, imperfectly developed—the percentage of nickel cells reaching and maintaining, approximately, the true osmotic pressure of the solution is greater than the percentage of copper cells.

CONCLUSION.

The results, appearing on the preceding pages, seem to justify the following important conclusion.

The Nickel Ferrocyanide membrane, as a means of measuring the osmotic pressure of solutions of Cane Sugar, is superior to the membrane of Copper Ferrocyanide..

BIOGRAPHY.

Lloyd Van Doren was born December 11, 1889 at New Germantown, N. J. His early education was received from the public schools of his home town. In the fall of 1903 he entered the preparatory department of Pennsylvania College, and two years later was admitted to the Collegiate department. In 1909 he graduated at Pennsylvania College receiving the degree of Bachelor of Science. The following fall he entered the graduate department of the Johns Hopkins University, majoring in Chemistry with Physical Chemistry and Applied Electricity as first and second subordinate subjects, respectively. In 1910-1911 he held a University scholarship and in June, 1911 was appointed a University Fellow for the year 1911-1912.